PORTLAND HARBOR RI/FS

FIELD SAMPLING PLAN
TRANSITION ZONE WATER SAMPLING

ADDENDUM 1
SAMPLING PLANS FOR EXXONMOBIL, GASCO, SILTRONIC, AND ARKEMA

March 27, 2006

Prepared for

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LIST OF ACRONYMS

bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, xylenes
COIs	chemicals of interest
CRBG	Columbia River Basalt Group
Cr(VI)	hexavalent chromium
DDX	combination of 4-4’ DDD, 4-4’ DDE, 4-4’ DDT
DRO	diesel range organics
FSP	field sampling plan
MCB	monochlorobenzene
MGP	manufactured gas production
MTBE	methyl-tert-butyl ether
PAHs	polycyclic aromatic hydrocarbons
QC	quality control
QAPP	quality assurance project plan
RI/FS	remedial investigation and feasibility study
RRO	residual range organics
SAP	sampling and analysis plan
TCE	trichloroethene
VOCs	volatile organic compounds

FOREWORD

This document is Addendum 1 to the Transition Zone Water Field Sampling Plan (Integral 2005b), which is Attachment 2 to the Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan (Integral et al. 2005). This addendum presents the site-specific sampling plans for collection of transition zone water samples from sediments in zones of potential discharge of groundwater chemicals of interest offshore of four sites along the Willamette River – ExxonMobil, Gasco, Siltronic, and Arkema. This final draft of Addendum 1 has been prepared following completion of the subject field work (completed December 2, 2005) to provide a complete and final document, which reflects the modifications to the sampling effort agreed upon for conditional approval by EPA and its agency partners. This conditional approval to proceed with the field work was provided on September 30, 2005 (EPA 2005).

1. INTRODUCTION

This document is Addendum 1 to the Transition Zone Water Field Sampling Plan (FSP; Integral 2005b), which is Attachment 2 to the Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan (SAP; Integral et al. 2005). This addendum presents the site-specific sampling plans for collection of transition zone water samples from sediments in zones of potential discharge of groundwater chemicals of interest (COIs) offshore of four sites along the Willamette River – ExxonMobil, Gasco, Siltronic, and Arkema.

This sampling will be conducted to support the Round 2 Groundwater Pathway Assessment for the Portland Harbor remedial investigation and feasibility study (RI/FS). Specific sampling methods and quality control protocols for the sampling and analyses are described in the FSP (Integral 2004) and the Supplement to Addendum 3 to the Quality Assurance Project Plan (QAPP; Integral 2005c).

Sampling plans for each site were developed based on consideration of multiple lines of evidence regarding potential areas of groundwater plume discharge, specifically:

- In-water temperature and conductivity mapping using the Trident system
- In-water seepage meter measurements
- Nature and extent of COIs in upland groundwater
- Groundwater flow gradients (horizontal and vertical)
- Upland and in-water stratigraphy
- Surface sediment texture mapping
- Transition zone water COI concentrations from screening samples collected during the discharge mapping effort (selected sites only)
- Available bulk sediment chemistry and toxicity data.

The findings of the August 2005 groundwater discharge mapping effort are presented for each site, along with relevant supporting information. The groundwater discharge mapping effort included stratigraphic coring, transect-based discharge mapping (temperature and conductivity measurement using the Trident Probe), and discharge verification measurement using seepage meters. The scope and methods of the groundwater discharge mapping effort are detailed in the Groundwater Discharge Mapping FSP (Integral 2005a), which is Attachment 1 to the SAP. To identify probable zones of groundwater discharge, the discharge mapping data are evaluated in the context of site upland and in-water hydrogeologic and chemical data, which are described in the SAP (Integral et al. 2005). Additional site-specific background information is presented in detail in Appendix A of the SAP. Sampling plans for the other five sites identified in the SAP and Transition Zone Water FSP will be provided in Addendum 2 to the FSP.

The following sections present the transition zone water sampling plans for each of the four sites and include a summary of the results of the discharge mapping findings, a map of the planned transition zone water sample locations, and a table summarizing sample counts, target sampling depth intervals, and COIs to be analyzed. In addition, each section discusses the rationale supporting the selection of the proposed sampling locations for each site.

2. EXXONMOBIL

2.1. SITE HYDROGEOLOGY AND COI MIGRATION

Figures 2-1, 2-2a, and 2-2b depict the potentiometric surface in the shallow water-bearing zone and geologic cross-sections at the ExxonMobil Site. Primary COIs in groundwater are those commonly associated with hydrocarbon releases, including benzene, toluene, ethylbenzene, xylenes (BTEX), methyl-tert-butyl ether (MTBE), polycyclic aromatic hydrocarbons (PAHs), and several metals. Figures 2-3a through 2-3d depict concentrations of total BTEX, lead, zinc, and arsenic in shallow groundwater. Figures 2-4a through 2-4c present the most recent groundwater concentration data[1] for upland wells on ExxonMobil cross-section C-C'.

Groundwater COI migration associated with the ExxonMobil site occurs in the shallow water-bearing zone of sand and sand/silt that underlies the site. Groundwater flow and discharge to the river is strongly influenced by the presence of a slurry wall. The slurry wall runs along the majority of shoreline from the site's southern border, but is absent along the northernmost ~200 ft of shoreline. This slurry wall is keyed into the silt/clay unit that underlies the shallow water-bearing zone. Groundwater flow is primarily toward the northern border of the site where the slurry wall is absent. As a result, it is expected that the majority of groundwater COI discharge occurs near the northern border in the nearshore sediments where the shallow water-bearing zone intersects with the Willamette River. This is further supported by the presence of BTEX, metals, and TPH in the shallow saturated zone in nearshore wells in this area (Figures 2-4a through 2-4c). A detailed discussion of the ExxonMobil Oil Terminal is presented in Appendix A-3 of the SAP (Integral et al. 2005).

2.2. ROUND 2 GROUNDWATER DISCHARGE MAPPING

The Trident Probe temperature and conductivity data, as well as relevant field observations (e.g., sediment texture), are summarized in Table 2-1. Temperature and conductivity mapping locations and results are shown on Figures 2-5 and 2-6. The groundwater discharge mapping effort primarily focused on the area at the northern end of the site where the slurry wall is absent, and thus, the potential for groundwater COI discharge to the Willamette River is expected to be greatest. Additional discharge mapping data were collected offshore of an abandoned former wooden sewer line on the south side of the dock area, as well as at several locations offshore of the slurry wall, to evaluate whether a potential pathway for groundwater COI migration to the river may exist in the form of a remnant plume.

The sediment texture offshore of the ExxonMobil site was recorded at each Trident location based on the resistance felt by the operators during the installation of the

[1] Note: All data for the cross-section plots were taken from Appendix A of the Groundwater Pathway Assessment SAP (Integral et al. 2005).

Trident Probe (Table 2-1). Confirmation surface sediment core samples (1-2 ft) were collected at four of the 43 Trident Probe locations to verify the operator observations. In addition, at 18 locations, the sediment was found to adhere to the probe upon removal, and the sediment texture was subsequently recorded. Figures 2-5 and 2-6 present the interpreted distribution of offshore sediment textures based on the Trident observations and from textures recorded in grab samples during the discharge mapping and past sediment sampling events. Several zones of surficial sand are present along portions of the site shoreline. Surface sediment texture grades to a fairly continuous zone of silty-sand to sandy-silt farther offshore. At the most offshore mapping locations, sediments tend to be silt.

Figures 2-5 and 2-6 present the Trident Probe results. Temperature (◦C) and conductivity (mS/cm) data are presented as the difference between simultaneous readings in the river water column (taken 30 cm above the sediment mudline) and the saturated sediment (taken 60 cm below the sediment mudline). In general, the ExxonMobil site displayed the same general patterns as those observed during the Groundwater Pathway Assessment Pilot Study (Integral 2005b,c), with the nearshore sands generally showing smaller temperature and conductivity differences and the offshore silts showing greater differences. It is hypothesized that the smaller temperature and conductivity differences observed in sand are the result of greater mixing between groundwater and surface water in coarser- versus finer-grained sediments.

Exceptions to this general pattern were observed at locations EM3-A, EM4-A, and EM8-A. These exceptions may indicate areas of higher groundwater flux to the river and a resulting suppression of the effects of mixing with surface water on transition zone water temperature and conductivity. This suppression would result in greater temperature and conductivity differences than those observed in other coarse-grained sediments where groundwater discharge to the river is less significant. The anomaly in the Trident temperature data at EM8-A suggests a potential area of higher groundwater discharge in the nearshore area near the southern end of the dock structure, where the former wooden sewer pipe was located.

Seepage meters were installed at six of the Trident locations offshore of the ExxonMobil site: EM1-A, EM1-D, EM3-A, EM3-D, EM5-A, and EM-11A. These seepage meter locations are designated EMSEEP 1A, EMSEEP 1D, EMSEEP 3A, EMSEEP 3D, EMSEEP 5A, and EMSEEP 11A. Complete results of the seepage meter measurements are presented in Figure 2-7; average and maximum observed fluxes at each location are also shown on Figures 2-5 and 2-6. The seepage meter measurements are consistent with the observed sediment textures, the conceptual model of hydrology and groundwater flow at the site, and the Trident mapping results. Specifically, average specific discharge rates of 4.0 to 9.8 cm/d were measured at locations in the nearshore sand and sand/silt, whereas average specific discharge rates of -18.9 to 1.2 cm/d were measured in the siltier materials farther offshore and at location EM-11A (which is located offshore of the slurry wall). This finding is consistent with the understanding of the site hydrogeology, which suggests that the surficial water-bearing unit intersects the river near the site shoreline, north of the slurry wall. The combined lines of evidence suggest that the shallow groundwater and associated COI discharge are likely occurring primarily through the nearshore sand zones.

2.3. TRANSITION ZONE WATER AND BULK SEDIMENT SAMPLING PLAN

Figure 2-8 presents the planned transition zone water sampling locations. A total of 17 transition zone water samples will be collected from 10 locations. At each location, a sample will be collected within the top 30 cm of the sediments. A second sample will be collected from a target depth of at least 90 cm (up to 150 cm, if possible) at seven of the locations. The rationale for the sampling locations is as follows:

- Samples will be collected from six locations (EM1-A, EM2-A, EM3-A, EM4-A, EM5-A, and EM6-B) in the nearshore sand and sand/silt sediments adjacent to the northern end of the site where the potential for groundwater COI discharge is likely the greatest. Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm, if possible) will be collected at four of these locations (EM1-A, EM2-A, EM3-A, and EM5-A).
- Samples will be collected from two locations (EM8-A and R2-EM-1) that are located farther to the south along the site shoreline to evaluate the potential for COI discharge associated with the abandoned former sewer line and a remnant plume that may be present offshore of the slurry wall. Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm, if possible) will be collected at location EM8-A, where an anomalous Trident temperature difference was recorded—suggesting that preferential groundwater discharge may be occurring in this area.
- Samples will be collected at two locations (EM2-C[2] and EM4-C) farther offshore at the northern end of the site. This sampling is being performed by agreement with EPA and its partners (EPA 2005) to provide information further offshore for reference and to support data interpretation. Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm, if possible) will be collected at both locations.

It is anticipated that the majority of the samples will be collected using the Trident Probe. Small-volume peepers will be used at any 30 cm location where the recovery (flow rate and/or volume) of the transition zone water by the Trident Probe is found

[2] By agreement with EPA on 9/30/05 (EPA 2005), due to limited availability of small-volume peeper sampling devices, location EM2-C was added to the sampling list with a contingency. The contingency specified that if attempts to sample EM2-C at 30 cm using the Trident fail, no attempt will be made at this station to sample with small-volume peepers.

to be inadequate. Replicate and equipment blank quality control (QC) samples will be collected in accordance with the specifications prescribed in the QAPP supplement (Integral 2005c).

Figure 2-8 also depicts the locations where bulk sediment samples will be collected to address sediment characterization data gaps in the vicinity of transition zone water sampling locations (EM2-A, EM3-A, and EM5-A). The sediment samples will be collected from transition zone water sampling locations where bulk sediment chemistry data results are not available for a similar sediment type located within approximately 50 ft. Round 2 sediment sampling locations are shown on Figure 2-8 for reference, and locations where volatile organic compound (VOC) analyses and/or toxicity bioassays were conducted on the sediment samples are indicated in unique colors.

Table 2-2 summarizes the analytes for the transition zone water and sediment samples.

3. GASCO

3.1. SITE HYDROGEOLOGY AND COI MIGRATION

Figures 3-1, 3-2a, and 3-2b depict the potentiometric surface in the shallow water-bearing zone and geologic cross-sections at the Gasco site. The general site stratigraphy at the Gasco site from the ground surface downward consists of a surficial fill unit, alluvial deposits, and the Columbia River Basalt Group (CRBG). This stratigraphy largely parallels that of the Siltronic site, located immediately upriver. Figures 3-3b through 3-3d depict concentrations of total BTEX, naphthalene, and dissolved lead in shallow groundwater. Figures 3-4a through 3-4h present the most recent groundwater concentration data[3] for upland wells on Gasco cross-sections A-A’ and B-B’.

At the Gasco site, relatively high concentrations of COIs (e.g., PAHs, BTEX, and metals) have been identified in groundwater both within the surficial fill and the alluvial deposits beneath the site. The highest COI concentrations in groundwater within the alluvial deposits occur beneath the former tar pond area in southeastern portion of the site, while the highest concentrations in the fill occur in the southwestern portion of the site. Vertical profiling of groundwater COI concentrations with depth through the alluvial zone suggest that COIs are migrating at depth, often at depths well below the river bottom. This is shown in Figures 3-4a through 3-4h. Additional detail is provided in Appendix A-4 of the SAP (Integral et al. 2005).

Groundwater in the surficial fill generally flows toward the river. A silt layer underlies a majority of the fill, becoming thin to absent toward the shoreline and then thicker at the shoreline and offshore (Figure 3-2b). In upland areas, a downward vertical groundwater gradient is typically observed between the fill and the underlying alluvium. Consequently, groundwater in the fill can be expected to migrate to the alluvium in areas where the underlying silt unit is absent and downward flow is not impeded.

Groundwater flow in the alluvial deposit is also toward the river, with the majority of the flow likely occurring in the more permeable sands/silty-sands. It is probable that the fine-grained silt, where present, impedes nearshore discharge of groundwater to the river. A similar silt layer is also present offshore of the Siltronic site. The findings of Siltronic’s 2004 and 2005 in-water investigation (using direct-push techniques; MFA 2005) suggest that discharge of COIs to the river associated with deeper groundwater flow may occur farther offshore beyond the silt layer (see Figures 4-5 and 4-6). NW Natural is currently planning a similar in-water investigation to explore the potential for deep groundwater COI discharge at the Gasco site.

[3] Note: All data for the cross-section plots were taken from Appendix A of the Groundwater Pathway Assessment SAP (Integral et al. 2005).

3.2. ROUND 2 GROUNDWATER DISCHARGE MAPPING

The Trident Probe temperature and conductivity data, as well as relevant field observations (e.g., sediment texture), are summarized in Table 3-1. Temperature and conductivity mapping locations and results are shown on Figures 3-5 and 3-6. The mapping locations focused on the nearshore area across the length of the site to better understand the extent of the offshore silt layer and evaluate its effect on shallow groundwater discharge. Of particular interest was the central to southeastern portion of the site, where groundwater COIs originating from both the Gasco and Siltronic sites are observed at high concentrations in upland groundwater samples. Potential groundwater COI discharge associated with deep groundwater flow from the Gasco site will be explored as part of NW Natural's upcoming in-water investigation.

The sediment texture offshore of the Gasco site was recorded at each Trident location based on the resistance felt by the operators during the installation of the Trident Probe. Confirmation grab samples of the sediment were collected at six of the 44 Trident measurement locations to verify operator observations. Additionally, when the sediment was found to adhere to the probe upon removal, its texture was subsequently recorded. Figures 3-5 and 3-6 present the interpreted distribution of offshore sediment textures based on the Trident observations, recent core samples, and past sediment sampling events. A notable feature of the sediment texture map is the laterally continuous zone of sand along the shoreline, which extends from transect GSC3 upstream to GSC7. This zone was not observed at transect GSC8, but reoccurs at the Siltronic site immediately upstream. Farther offshore, the surface sediment texture trends toward sandy-silt and silt.

Figures 3-5 and 3-6 present the Trident Probe results. Temperature (◦C) and conductivity (mS/cm) data are presented as the difference between simultaneous readings in the river water column (taken 30 cm above the sediment mudline) and the saturated sediment (taken 60 cm below the sediment mudline). In general, the Gasco site displayed the same general patterns as those observed during the Groundwater Pathway Assessment Pilot Study (Integral 2005a,b), with the nearshore sands generally showing smaller temperature and conductivity differences and the offshore silts showing greater differences. It is hypothesized that the smaller temperature and conductivity differences observed in sand are the result of greater mixing between groundwater and surface water in coarser- versus finer-grained sediments. Exceptions to this general pattern were observed at transects GSC4 through GSC7, with many of the nearshore sand locations (e.g., GSC5-B) displaying greater temperature differences than other nearby transect locations in similar sediment types. These results may indicate areas of higher groundwater flux and a resulting suppression in the effects of mixing with surface water on transition zone water temperature and conductivity.

Seepage meters were installed at eight of the Trident Probe locations offshore of the Gasco site: GSC2-A, GSC3-A, GSC4-A, GSC4-C, GSC4-E, GSC7-B, GSC7-D, and GSC7-F. These seepage meter locations are designated as GCSEEP 2A, GCSEEP

3A, GCSEEP 4A, GCSEEP 4C, GCSEEP 4C, GCSEEP 4E, GCSEEP 7B, GCSEEP 7D, and GCSEEP 7F.[4] Due to significant sediment de-gassing during the seepage meter measurements, only limited data could be collected from location GSC7-B. Further, no data could be collected at GCSEEP 7D due to an equipment failure.[5] The results of the seepage meter measurements are presented in Figure 3-7; average and maximum observed fluxes at each location are also shown on Figures 3-5 and 3-6. The average specific-discharge rates ranged from -2.1 to 5.7 cm/d. The discharge rates measured at the majority of the locations were low (<1 cm/d). The greatest discharge rate was recorded at GCSEEP 7B, where average and maximum specific discharge rates of 5.7 and 8.7 cm/d were recorded, respectively. A continuous positive flux was also recorded at location GCSEEP 3A, where average and maximum specific discharge rates of 3.7 and 6.0 cm/d were recorded, respectively.

Results of the seepage measurements and Trident mapping are generally consistent, and suggest some groundwater discharge from the shallow water-bearing zone may be occurring through the nearshore sediments adjacent to the Gasco site. The Trident and seepage meter data, combined with upland groundwater data, suggest that contaminated groundwater discharge may be greatest offshore of the southeast (upstream) half of the site. The potential for COI discharge farther offshore associated with deeper groundwater flow will be evaluated during NW Natural's upcoming in-water investigation.

3.3. TRANSITION ZONE WATER AND BULK SEDIMENT SAMPLING PLAN

Figure 3-8 presents the planned transition zone water sampling locations. A total of 16 transition zone water samples will be collected from 11 locations. At each location, a sample will be collected within the top 30 cm of the sediments. A second sample will be collected from a target depth of at least 90 cm (up to 150 cm, if possible) at five of the locations. The rationale for the sampling locations is as follows:

- Samples will be collected from six locations within or adjacent to the nearshore sand zone in the central/southern portion of the site (GSC4-A, GSC5-A, GSC5-B, GSC6-A, GSC7-B, GSC8-A). These locations are immediately offshore of the area where COI concentrations are elevated in upland shallow groundwater, focusing on areas of coarse-grained sediments where the potential for shallow groundwater COI discharge is likely to be the greatest. Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm,

4 Due to the proximity to the tar body, no seepage meters were placed on transect 5 and the potential to damage the equipment,.

5 A second attempt at recording seepage rates at location GCSEEP 7D could not be completed due to schedule limitations.

if possible) will be collected at three of these locations (GSC4-A, GSC5-A, and GSC7-B).

- Samples will be collected from two locations (GSC1-B and GSC2-A) in the nearshore area at the northern (downstream) portion of the site to evaluate the potential discharge of COIs present in upland groundwater in this portion of the site.
- Samples will be collected from three locations (GSC6-D, GSC7-D and GSC8-D) in the silty area offshore from the nearshore sand unit to provide a point of reference for transition zone water concentrations in areas where groundwater discharge may not be occurring. Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm, if possible) will be collected at GSC7-D and GSC8-D.

It is anticipated that the majority of the samples will be collected using the Trident Probe. Small-volume peepers will be used at any locations where the recovery (flow rate and/or volume) of the transition zone water by the Trident Probe at 30 cm is found to be inadequate. Replicate and equipment blank QC samples will be collected in accordance with the specifications prescribed in the QAPP supplement (Integral 2005c).

Figure 3-8 also depicts the locations where bulk sediment samples will be collected to address sediment characterization data gaps in the vicinity of transition zone water sampling locations (GSC4-A, GSC7-B, and GSC7-D). The sediment samples will be collected from transition zone water sampling locations where bulk sediment chemistry data results are not available for a similar sediment type located within approximately 50 ft. Round 2 sediment sampling locations are shown on Figure 3-8 for reference, and locations where VOC analyses and/or toxicity bioassays were conducted are indicated in unique colors.

Table 3-2 summarizes the analytes for the transition zone water and sediment samples.

4. SILTRONIC

4.1. SITE HYDROGEOLOGY AND COI MIGRATION

Figures 4-1, 4-2a, and 4-2b depict the potentiometric surface in the shallow water-bearing zone and geologic cross-sections at the Siltronic site. The general site stratigraphy at the Siltronic site largely parallels that of the Gasco site (see Section 3.1) and consists, from the ground surface downward, of a surficial fill unit, a laterally discontinuous silt unit, an alluvial water-bearing zone, and the CRBG (Figures 4-2a and 4-2b). The general direction of groundwater flow is north-northeast toward the Willamette River. Figures 4-3b and 4-3c depict concentrations of total BTEX and trichloroethene (TCE), respectively, in shallow groundwater. Figures 4-4a through 4-4d present the most recent groundwater concentration data[6] for upland wells on Siltronic cross-sections A-A' and B-B'.

Near the river, TCE and degradation products are present in groundwater in the intermediate zone of the alluvial aquifer [80-140 ft below ground surface (bgs)]. Manufactured gas production (MGP) waste and dense non-aqueous phase liquid (DNAPL) have been observed in subsurface investigations in the former tar pond areas at the Siltronic site. BTEX in groundwater at the Siltronic site is primarily associated with the surficial fill water-bearing zone, but extends into the alluvial aquifer in the northwestern portion of the site, as shown on Figures 4-4a and 4-4b. A deeper contaminated zone, characterized by COIs that appear to be associated with offsite sources (dichlorobenzene and Silvex), is present in the lower alluvial aquifer (166-207 ft bgs). The highest concentrations of TCE and BTEX tend to occur in groundwater beneath the western portion of the site, near the common site border with the Gasco site. Vertical profiling of groundwater COI concentrations with depth through the alluvial zone (Figures 4-4a and 4-4c) suggest that much of the COI mass is migrating at depth, often below the river bottom. Additional detail is presented in Appendix A-5 of the SAP (Integral et al. 2005).

The cross-sections shown in Figure 4-4a and 4-4c suggest a possibility of shallow groundwater discharge to the river through the fill and nearshore silty sand. The silt unit shown on Figure 4-4a may act as an aquitard in upland areas where observed, but it thins and becomes silt to silty sand toward the river. It should be noted that data from a 2004 in-water investigation (using direct-push techniques; MFA 2005) conducted offshore of the Siltronic site suggest that site groundwater COIs (TCE and degradation products) discharge to the river primarily farther offshore (i.e., where the outcrop of silt, shown in Figures 4-5 and 4-6, is absent). Several plan view images and one cross-section from the 2004 investigation are presented as Siltronic Supplemental Figures ES-1, ES-2, 5-2, and 5-4.

[6] Note: Data for the cross-section plots were taken from Appendix A of the Groundwater Pathway Assessment SAP (Integral et al. 2005).

4.2. ROUND 2 GROUNDWATER DISCHARGE MAPPING

The Trident Probe temperature and conductivity data, as well as relevant field observations (e.g., sediment texture), are summarized in Table 4-1. Mapping of transition zone water temperature and conductivity using the Trident Probe was conducted in the nearshore area on the northwest side of the site to better understand the extent of the offshore silt layer and to evaluate its effect on shallow groundwater discharge. Temperature and conductivity mapping locations and results are shown on Figures 4-5 and 4-6. In addition, samples of transition zone water were collected from five of the Trident locations (SLT1-B, SLT2-A, SLT3-A, SLT4-A, and SLT5-A) for screening of TCE, TCE degradation products, and BTEX as indicators of groundwater discharge.[7]

The sediment texture offshore of the Siltronic site was recorded at each Trident location based on the resistance felt by the operators during the installation of the Trident Probe. Confirmation grab samples of the sediment were collected at five of the 29 total Trident locations to verify the operator observations. In addition, at 12 locations, the sediment was found to adhere to the probe upon removal, and the sediment texture was subsequently recorded. Figures 4-5 and 4-6 present the interpreted distribution of offshore sediment textures based on the Trident observations, recent core samples, and past sediment sampling events. A notable feature of the sediment texture map is a laterally continuous zone of sand along the shoreline, which extends from transect SLT1 upstream to transect SLT5. This feature is similar to the nearshore sand observed between transects GSC3 and GSC7 at the Gasco site, located immediately downriver. Farther offshore, the surface sediment texture trends to sandy-silt and silt.

Figures 4-5 and 4-6 present the Trident Probe results. Temperature (◦C) and conductivity (mS/cm) data are presented as the difference between simultaneous readings in the river water column (taken 30 cm above the sediment mudline) and the saturated sediment (taken 60 cm below the sediment mudline). The Siltronic site displayed the same general patterns as those observed at other sites along the river during the Groundwater Pathway Assessment Pilot Study (Integral 2005a,b), with the nearshore sands typically showing smaller temperature and conductivity differences and the offshore silts showing greater differences. It is hypothesized that the smaller temperature and conductivity differences observed in sand are the result of greater mixing between groundwater and surface water in coarser- versus finer-grained sediments. Some exceptions to this general pattern were noted. Locations SLT2-C, SLT3-C, and SLT4-A all displayed larger than expected temperature differences when compared to similar locations at the site. These results may indicate areas of higher groundwater flux and a resulting suppression in the effects of mixing with surface water on transition zone water temperature and conductivity.

[7] Collection of transition zone water samples for screening analysis was attempted at eight locations; however, three locations (SLT2-C, SLT3-B, and SLT4-C) yielded inadequate flow rates (<2 mL/min) to prevent loss of volatiles during VOC sample collection.

Seepage meters were installed at six of the Trident locations offshore of the Siltronic site: SLT2-A, SLT2-C, SLT2-E, SLT3-A, SLT4-A, and SLT4-B. These seepage meter locations are designated as SLSEEP 2A, SLSEEP 2C, SLSEEP 2E, SLSEEP 3A, SLSEEP 4A, and SLSEEP 4B. Complete results of the seepage meter measurements are presented in Figure 4-7; average and maximum observed fluxes at each location are also shown on Figures 4-5 and 4-6. In agreement with Trident mapping results, locations SLSEEP 4A and SLSEEP 2C showed the highest average discharge rates (10.5 cm/d and 5.1 cm/d, respectively). Locations SLSEEP 2A and SLSEEP 3A fluctuated between high relative rates of discharge (positive flux) to high relative rates of recharge (negative flux). As a result, the average specific discharge rates at locations SLSEEP 2A and SLSEEP 3A were not high (0.2 and 0.3 cm/d, respectively), despite the fact that relatively high, positive maximum specific discharge rates (18.5 and 2.2 cm/d, respectively) were recorded at these locations. Location SLSEEP 4B, which is located in the silt, showed primarily negative flux signals, suggesting that river water may be locally recharging at this location. In contrast, location SLSEEP 2E, which is located offshore in a silt to mixed sand/silt zone, showed a positive average flux of 3.5 cm/d.

Screening samples of transition zone water were collected for analysis of VOCs at locations[7] SLT1-B, SLT2-A, SLT3-A, SLT4-A, and SLT5-A during the August 2005 discharge mapping field effort. All of these screening sample locations are inshore of the transition zone water impacts areas shown on Siltronic Supplemental Figures ES-1 and ES-2. The screening sample results are presented on Figure 4-8 and in Table 4-2. The data show low concentrations of total BTEX in two of the samples, SLT1-B and SLT4-A (14.1 and 26.8 µg/L, respectively). Other samples had even lower total BTEX results, at or near detection limits, ranging from 0.6 to 2.7 µg/L total BTEX. Results for all screening locations were below detection limits for TCE, 1,2-DCE, and vinyl chloride. This finding supports the conceptual understanding of the shallow groundwater COIs at the site, and is in agreement with nearshore discharge mapping results. Specifically, location SLT1-B is near the northwest boundary of the site where there are known NAPL sources in the groundwater. Location SLT4-A is located immediately offshore of well P-2, in which 61 µg/L of total BTEX was detected in shallow groundwater in the most recent published results (Figure 4-4b). Further, Trident readings indicate that greater relative groundwater discharge may be occurring at location SLT4-A—a finding that was confirmed by collocated seepage meter results (Figure 4-5).

Overall, these findings suggest that groundwater is likely discharging through this nearshore sand zone as well as further offshore through the siltier zones (see seepage meter results for SLSEEP2C and SLSEEP2E (Figure 4-5).

4.3. TRANSITION ZONE WATER AND BULK SEDIMENT SAMPLING PLAN

Figure 4-9 presents the planned transition zone water sampling locations. A total of 14 transition zone water samples will be collected from 11 locations. At each location, a sample will be collected within the top 30 cm of the sediments. A second sample will be collected from a target depth of at least 90 cm (up to 150 cm, if possible) at three of the locations. The rationale for the sampling locations is as follows:

- Samples will be collected from five locations within the nearshore sand zone at the northern end of the site where the potential for shallow groundwater COI discharge is likely the greatest (SLT1-A, SLT2-A, SLT3-A, SLT4-A, and SLT5-A), based on the seepage data and Trident mapping. Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm, if possible) will be collected at two of these locations (SLT2-A and SLT4-A).
- Samples will be collected from two locations (SLT2-C and SLT3-C) in the silty area offshore from the nearshore sand unit to assess possible groundwater seepage indicated by seepage meter SLSEEP2C and Trident results.
- Samples will be collected from four locations (SLT1-E, SLT2-E, SLT3-F, and SLT4-F) farther offshore near the break in slope to the navigation channel. These locations partially overlap the locations of transition zone water and offshore groundwater sampling performed by Siltronic in 2004 and 2005 (see Siltronic Supplemental Figures 1 through 4). Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm, if possible) will be collected at one of these locations (SLT3-F).

It is anticipated that the majority of the samples will be collected using the Trident Probe. Small-volume peepers will be used at any locations where the recovery of the transition zone water at 30 cm below the sediment surface by the Trident Probe is found to be inadequate. Replicate and equipment blank QC samples will be collected in accordance with the specifications prescribed in the QAPP supplement (Integral 2005c).

Figure 4-9 also depicts the locations where bulk sediment samples will be collected to address sediment characterization data gaps in the vicinity of transition zone water sampling locations (SLT2-A, SLT2-E, SLT3-F, SLT4-A, SLT4-F, and SLT5-A). The sediment samples will be collected from transition zone water sampling locations where bulk sediment chemistry data results are not available for a similar sediment type located within approximately 50 ft. Round 2 sediment sampling locations are shown on Figure 4-9 for reference, and locations where VOC analyses and/or toxicity bioassays were conducted are indicated in unique colors.

Table 4-3 summarizes the analytes for the transition zone water and sediment samples.

5. ARKEMA

5.1. SITE HYDROGEOLOGY AND COI MIGRATION

Figures 5-1, 5-2a, 5-2b, and 5-2c depict the potentiometric surface in the shallow water-bearing zone and geologic cross-sections at the Arkema site. Figures 5-3b through 5-3g depict concentrations of total chromium, perchlorate, 4-4' DDD, 4-4' DDE, 4-4' DDT, and chlorobenzene in shallow groundwater. Supplemental Figures 11 and 14 depict concentrations of chlorobenzene and 4-4' DDT in offshore groundwater measured during in-water investigations performed by Arkema (formerly ATOFINA) in 2002 and 2003 (Integral 2003). Figures 5-4a through 5-4m present the most recent groundwater concentration data[8] for upland wells on Arkema cross-sections.

Above the basalt bedrock, groundwater at the Arkema site occurs in up to three sandy zones separated by laterally discontinuous silt layers (Figures 5-2a, 5-2b, and 5-2c). Distinction between these layers is more apparent in the former Acid Plant area, and less so in the former Chlorate Plant area. In general, the groundwater flow direction is toward the river. The primary pathway of concern for upland groundwater plumes to reach the river is through the shallow to intermediate aquifer zones present at both the former Acid Plant and Chlorate Plant areas.

There are four dissolved plumes of groundwater COIs at the site, as shown on Figures 5-3a through 5-3g. The DDT and monochlorobenzene (MCB) plumes overlap in the Acid Plant area and are present in nearshore wells. In the former Chlorate Plant area, hexavalent chromium [Cr(VI)] and perchlorate plumes overlap and are present in the nearshore wells. A residual MCB DNAPL source area is present in the shallow zone within the former Acid Plant area. The MCB NAPL source area is present in the form of microglobules rather than as a continuous, pore-filling phase (ERM 2002); consequently, it is not expected to migrate significantly in the NAPL phase. As shown in Figures 5-4a through 5-4n, MCB is present in groundwater offshore of the former Acid Plant area in both silt and sand layers of sediment. Further, as shown in these cross-sections, DDT impacts to groundwater extend offshore of the site near Dock 1 and Dock 2 of the former Acid Plant area. Potential migration of these COIs to shallow sediments and, ultimately, to the river will be assessed through transition zone water sampling, as planned in this document. Additional detail is provided in Appendix A-7 of the SAP (Integral et al. 2005).

5.2. ROUND 2 GROUNDWATER DISCHARGE MAPPING

Temperature and conductivity mapping data were collected at Arkema during the Groundwater Pathway Assessment Pilot Study (Integral 2005a and 2005b) in November 2004. Specifically, Trident measurements were taken at 41 points distributed over 11

[8] Note: All data for the cross-section plots were taken from Appendix A of the Groundwater Pathway Assessment SAP (Integral et al. 2005).

transects across the nearshore areas of the former Acid Plant and the former Chlorate Plant, as shown on Figures 5-5 and 5-6. The sediment textures offshore of the Arkema site were recorded at each Trident location based on the resistance felt by the operators during the installation of the Trident Probe. Figures 5-5 and 5-6 present the interpreted distribution of offshore sediment textures based on the Trident observations and past sediment sampling events. A laterally continuous zone of sand is evident along most of the shoreline, though it appears to be absent offshore of the Chlorate Plant area in the vicinity of transects CP8 and CP9. Farther offshore, the sediment texture trends toward mixed sand/silt and silt. However, based on stratigraphic data, and as shown in the cross-sections presented in Figures 5-2a and 5-2b, sandier water-bearing materials may also be in hydraulic communication with the river farther offshore, in the vicinity of and immediately offshore of the dock structures.

Figures 5-5 and 5-6 present the Trident Probe results as the difference in temperature (◦C) and conductivity (mS/cm) between the river water and the sediments (at a depth of 60 cm) from the 2004 pilot study (Integral 2005a,b). In general, the nearshore sands generally showed smaller temperature differences, and the offshore silts showed greater differences. Apparent exceptions to this general pattern were observed at locations CP-07-B and CP-11-AA, where temperature signals in the nearshore sand were stronger than elsewhere. These exceptions may indicate areas of higher groundwater flux and a resulting suppression in the effects of mixing with surface water on transition zone water temperature.

At the Arkema site, a strong conductivity signal was observed at most locations. Very high conductivity readings, up to 92 mS/cm (for context, this high conductivity reading is roughly twice that of typical seawater), were observed in the Arkema sediments (Figure 5-6). These may be associated with either groundwater discharge, historical over-water releases in the vicinity of the salt dock, or both.

In addition to the Trident Probe measurements, transition zone water samples were collected from six locations at the Arkema site during the pilot study using various methods. Specifically, three samples were collected offshore of the Acid Plant (AP03B, AP04B, and AP04D; Figure 5-5), and three more were collected offshore of the Chlorate Plant (CP06C, CP07B, and CP08D; Figure 5-5). Locations AP03B and CP07B, both within sandy sediments, showed strong temperature signals relative to similarly situated locations. This potentially indicated areas of focused groundwater discharge. This indication was verified by seepage rate measurements recorded during the pilot study, which demonstrated that groundwater discharge at CP07B was positive and greater than at the other two locations evaluated (AP04B and AP04D; Figures 5-5 and 5-6).

The surface sediments at the other pilot study transition zone water sampling locations (AP04B, AP04D, CP06C, and CP08D) are characterized by silt and mixed sand/silt. Seepage rates at AP04B showed a very low net positive discharge to the river, while AP04D seepage rates showed no average positive discharge over the 24-hr deployment period. These results are consistent with the presence of a fine-grained aquitard underlying the shallow water-bearing zone (Figure 5-2b), limiting the potential for groundwater discharge offshore of the nearshore sands. The highest concentrations of perchlorate and chromium in transition zone water were found at CP07B, consistent with the interpretations of the groundwater discharge mapping data from the pilot study, as presented in the Discharge Mapping FSP (Integral 2005a). The elevated concentrations of VOCs and DDX (combination of 4-4' DDD, 4-4' DDE, 4-4' DDT) detected in transition zone water at AP03B are consistent with the higher rates of groundwater discharge at this location expected based on the Trident data and sediment texture observations.

During the August 2005 investigation, seepage meters were installed at 11 locations offshore of the Arkema site: APSEEP 1 through CPSEEP 11 (Figures 5-5 and 5-6). Complete results of the seepage meter measurements for these locations are presented in Figure 5-7. Average and maximum observed fluxes at each of these locations, as well as at the three locations evaluated during the 2004 pilot study, are shown on Figures 5-5 and 5-6. Near the shoreline, sandy and silty-sand locations APSEEP 1, APSEEP 5, CPSEEP 10, and CPSEEP 11 displayed high discharge rates relative to other locations, with average specific discharge rates of 4.0, 3.1, 7.0, and 2.1 cm/d, respectively. The maximum specific discharge rates recorded at these locations were 16.0, 17.4, 31.5, and 3.1 cm/d, respectively. The average specific discharge rate at the remaining locations was low (<0.5 cm/d) or negative (recharge). In general, the nearshore sand and silty-sand sediments were found to have higher relative discharge rates, consistent with site stratigraphy and the conceptual model of shallow groundwater flow. The most offshore seepage meters (APSEEP 3, APSEEP 6, and CPSEEP 9), located slightly offshore of the dock structures, showed near-zero average discharge rates (ranging from 0.5 to -1.2 cm/day).

5.3. TRANSITION ZONE WATER AND BULK SEDIMENT SAMPLING PLAN

Figure 5-8 presents the planned transition zone water sampling locations. In the Acid Plant area, a total of 10 transition zone water samples will be collected from seven locations. In the Chlorate Plant area, a total of 11 transition zone water samples will be collected from eight locations. At each location, a sample will be collected within the top 30 cm of the sediments. A second sample will be collected from a target depth of at least 90 cm (up to 150 cm, if possible) from three locations in the Acid Plant area and three locations in the Chlorate Plant area. The rationale for the sampling locations is as follows:

- Samples will be collected from seven locations within the nearshore sand zone (AP-02-A, AP-03-A, CP-06-A, CP-07-A, CP-07-B, CP-08-B, and CP-09-A). Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm, if possible) will be collected at three of these locations (AP-03-A, CP-06-A, and CP-07-B). These sampling locations are focused on the nearshore sand to silty sand zones immediately offshore of the upland COI plumes, where the potential for shallow groundwater (and associated COI) discharge is the greatest.

- Samples will be collected from three locations (R2-AP-1, R2-AP-2, and AP-04-C) from intermediate depths inshore of the docks in the Acid Plant area. These are located in the region where the highest concentrations of chlorobenzene and DDT were observed during Arkema's offshore groundwater investigation (see Supplemental Figures 11 and 14 and Figures 5-4a through 5-4m), and where recorded seepage rates (APSEEP 5) suggest groundwater discharge may be occurring. Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm if possible) will be collected R2-AP-2.
- Samples will be collected from five locations (AP-02-D, AP-03-D, R2-CP-1, CP-07-D, and CP-09D) farther offshore near the break in slope to the navigation channel to evaluate potential COI discharge associated with deeper groundwater flow at the site. Paired samples at depths of 30 cm and at least 90 cm (up to 150 cm, if possible) will be collected at two of these locations (AP-03-D and CP-07-D).

Figure 5-8 also depicts the locations where bulk sediment samples will be collected to address sediment characterization data gaps in the vicinity of transition zone water sampling locations (AP-02-A, AP-02-D, AP-04-C, R2-AP-2, CP-07-A, CP-07-D, CP-09-A, and CP-09-D). The sediment samples will be collected from transition zone water sampling locations where bulk sediment chemistry data results are not available for a similar sediment type located within approximately 50 to 100 ft. Round 2 and historic sediment sampling locations are shown on Figure 5-8 for reference, and locations where VOC analyses and/or toxicity bioassays were conducted are indicated in unique colors.

It is anticipated that the majority of the samples will be collected using the Trident Probe. Small-volume peepers will be used at any locations where the recovery of the transition zone water at 30 cm below the sediment surface by the Trident Probe is found to be inadequate. Replicate and equipment blank QC samples will be collected in accordance with the specifications prescribed in the QAPP supplement (Integral 2005c).

Table 5-1 summarizes the analytes for the transition zone water and sediment samples.

6. REFERENCES

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